BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

As rescanning documents *will not* correct images, please do not report the images to the Image Problem Mailbox.

PCT WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 4 : G01N 31/16, 27/26 — A1

(11) International Publication Number: WO 88/ 07196

(43) International Publication Date: 22 September 1988 (22.09.88)

(21) International Application Number: PCT/HU88/00007

(22) International Filing Date: 4 February 1988 (04.02.88)

(31) Priority Application Number: 1059/87

(32) Priority Date: 11 March 1987 (11.03.87)

(33) Priority Country: HU

(71) Applicant: HAJTÓMŰVEK ÉS FESTŐBERENDEZÉSEK GYÁRA [HU/HU]; Fehérvári út 98, H-1522 Budapest XI (HU).

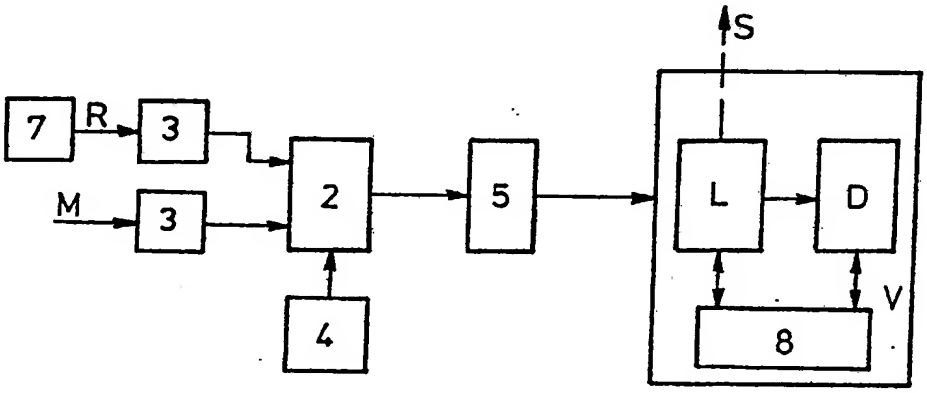
(72) Inventors: PUNGOR, Ernő ; Meredek u. 4, H-1112 Budapest (HU). SZEPESVÁRY, Tamásné ; Nánási út 46, H-1031 Budapest (HU). LINDNER, Ernő ; Kiscelli köz 4, H-1036 Budapest (HU). HORVAI, György ; Szemlőhegyi u. 20, H-1022 Budapest (HU). SÁRKÁNY, Péter ; Alkotás u. 13, H-1123 Budapest (HU). SLEZSÁK, István ; Bocskai u. 42, H-3770 Sajószentpéter (HU). HEGAJ, Szvetlana ; Eper u. 49, H-1112 Budapest (HU).

(74) Agent: PATENTBUREAU DANUBIA; P.O. Box 198, H-1368 Budapest (HU).

(81) Designated States: AT (European patent), BE (European patent), BG, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), LU (European patent), NL (European patent), RO, SE (European patent), SU.

Published
With international search report.

(54) Title: METHOD OF AND EQUIPMENT FOR DETERMINING CONCENTRATION OF A COMPONENT OF A LIQUID SAMPLE BY MEANS OF POTENTIOMETRY



(57) Abstract

For potentiometric determining the concentration of a component of a liquid sample the novel elements lie in further steps of admixing the titration reagent in a quantity deviating from the equivalence quantity by about 1 % to about 20 % in weight, determining the difference to the equivalence quantity by measurement of the electric potential of the electrode and comparing the potential value with a calibration diagram determined earlier and computing the concentration on the basis of the difference determined. As for the proposed equipment, comprising a unit (2) for receiving a liquid sample, a feeding unit (3) for introducing a titration reagent into the sample and measuring means (5) with an electrode held in contact with the sample containing the titration reagent, the novelty is determined by further comprising a mixer (4) for homogenising the sample, wherein the feeding unit (3) introduces a regulated quantity of a liquid into the sample and the measuring means (5) are connected to a linear amplifying and/or regulating unit (L).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	FR	France	ML	Mali
AU	Australia	GA	Gabon	MR	Mauritania
BB	Barbados	GB	United Kingdom	MW	Malawi
BE	Belgium	HU	Hungary	NL	Netherlands
BG	Bulgaria	IT	Italy	NO	Norway
BJ	Benin	JP	Japan	RO	Romania
BR	Brazil	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic			SE	Sweden
CG	Congo	KR	Republic of Korea	SN	Senegal
CH	Switzerland	LI	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
DE	Germany, Federal Republic of	LU	Luxembourg	TG	Togo
DK	Denmark	MC	Monaco	US	United States of America
FI	Finland	MG	Madagascar		

METHOD OF AND EQUIPMENT FOR DETERMINING CONCENTRATION OF A COMPONENT OF A LIQUID SAMPLE BY MEANS OF POTENTIOMETRY

The invention refers to a method of and an equipment for determining concentration of a component of a liquid sample by means of potentiometry. The method comprises the steps of admixing a titration reagent of known concentration in regulated quantities to a sample of known quantity, measuring the potential of an electrode contacting the liquid sample including the admixed titration reagent and determining the concentration on the basis of the measured potential. The equipment being capable of carrying the method, comprising a unit for receiving a liquid sample, a feeding unit for introducing a titration reagent into the liquid sample and measuring means including an electrode held in contact with the liquid sample containing the titration reagent, can be used for determining concentration of a component with accuracy which is high enough for practical purposes and for supplying electric signals applicable in controlling industrial processes.

When applying methods of potentiometry the measurement of the voltage is carried out in a measuring chamber for determining the concentration or activity value of a component of a sample. The methods with application of a titration reagent are those showing excellent accuracy among other methods.

The method of titration potentiometry is a kind of the volumetric analyse wherein the sample is admixed with a titration reagent of known concentration in parts of known quantity and the change of the concentration (activity) is followed by determining the potential of an indicating electrode. On this basis the concentration of the component reacting with the titration reagent can be determined.

The automatic titration apparatuses make it possible to reduce the high demand on time and work charac-

terizing the methods of potentiometric titration. Taking into account the fact that the potentiometric titration should generally be carried out for establishing the end point of the titration process amny efforst have been made for elaborating titration methods requiring the possible lowest number of measurement points. In the apparatuses for carrying out the titration it is possible to continue the progess up to reaching an earlier determined value of the potential (the end point potential)..

From the literature a method of acidic-basic titration is known (Ivaska, A.: Talanta, 21 /1974) 377, ibid 21 /1974) 387) which is similar to the end point titration but the process should be carried out up to reaching the same pH value, wherein the titration gradë is much lower than 100 %.

Johansson et al (Johansson, G., Backlin, W.: Anal. Chim. Acta, 69 /1974/ 415)(Aström, O. (Anal.Chim. Acta, 88 /1977/ 17 and Anal. Chim. Acta, 97 /1978/ 259)and other authors applied the mixture of weak acids to titrating strong bases and vica versa. By appropriate selection of the composition of the mixture it is possible to create conditions wherein the pH value of the titration reagent depends on the concentration of the sample to be titrated according to a linear function with slope being high enough to ensure the required accuracy of the measurements by only one determining of the pH value and the resulted concentration value is the true one with high reliability.

Many practical problems arising during the titration process made it necessary to modify the different potentiometric methods in order to carry out measurements in flowing samples. Some of these problems are the following:

— it is often necessary to follow continouosly the composition of samples in the time (for example in natural waters, in waste waters, during chemical reactions

and in biological systems);

— automatic analysis of a high number of samples and/ /or samples of small volume (for example in the medical laboratories, analysis of soil samples for agricultural purposes).

By applying electroanalitical detectors to measuring characteristics of samples held in flow it has been shown that the analysis carried out in flowing liquids is under some aspects very advantageous - the reproducibility of the measured potential values, the conditioning of the electrodes are more favorable than in systems with stationary liquids. An automatic apparatus for analysis to be carried out automatically in systems with flowing liquids is shown in the U.S. patent specification No. 3 484 170 (granted to the assignee Technicon Co.). Another possibility is to inject some of the liquids to the flow. Both methods result in considerable reduction of the duration of the measurements. An inadvantageous feature of these methods lie in relatively low accuracy in comparison to the titration methods.

By carrying the titration process in flowing samples it is possible to have the advantages of the previously mentioned solutions. In this case the regulation obviously relates to the volume flow rate and/or to the composition of the titration reagent which are controlled in a programmed way. A titration process with flowing samples having composition altered according to a linear time function is proposed by Eichler et al. (Eichler, D. L., Technicon Symposium, 1969, Vol. 1., Mediad, New York, 1970, p. 51.), by Fleet et al. (Fleet, B., Ho, A. Y. W.: Anal. Chem, 46 /1974) p. 9) and by the Hungarian Patent granted under No. 174 711 to Nagy G., Pungor E., Tóth K., Havas J. and Fehér Zs. The authors of the articles previously mentioned apply mechanical means for altering the composition of the solution according to a linear program and the Hungarian Patent proposes the

application of program controlled coulometric means for producing the necessary reagents. The apparatus proposed by Eichler et al. and by Fleet et al. is relatively complicated in use if more titration processes should be carried out one after another and the accuracy to be ensured can be sometimes not reached because of the impossibility of accurate determining the volume flow rate in the end point of the titration (this follows from the geometrical arrangement). The coulometric methods of producing the necessary reagents are generally expensive, they require many different means and the speed of determining is relatively low because of the necessity of taking two titration curves.

In controlling different processes it is often very important to maintain a stable value of the concentration wherein the accurate value is not known, its knowledge is not important. In such cases the analisators can be applied which make use of the features of the flow analysis and the titration to an end point. Such apparatus is shown e.g. in the Swiss patent specification No. 431 444 (granted in 1967 to Polymetron AG.). The apparatuses of this kind make a reagent aequivalent with a sample of optimal concentration and the sample flow in equal volume flow rates. They include a mixing chamber wherefrom the mixed liquid flow to a potentiometric detector chamber. The disadvantage of this method is that the voltage measured in the detector chamber is a nonlinear function of the concentration difference from the optimal value and this renders the solution of the control processes more difficult.

A further disadvantage of the preciously shown method and apparatus is that in this way it is practically impossible to determine the accurate value of the concentration of the sample, the only piece of information obtainable is whether the concentration is equal with the aequivalence value or in which direction differs from it. This uncertainty can result in very high oscillations of the concentration

on the beginning of the control process, these oscillations requiring complicated arrangement if the control process should be realised in automatic systems.

The invention is based on the recognition that the continuous determination of a component of a liquid sample can be realised with high (comparable with the titration methods) accuracy when a titration reagent of exactly known concentration is admixed to it wherein the concentration is selected to lie in a range for ensuring the titration grade about 90 to 95 % or 105 to 110 % on the basis of previous orientation measurements and the remaining part of the component to be determined or the surplus of the titration reagent is determined by a direct potentiometric measurement (without application of any further titration reagent). In this way the advantage of the high speed characterizing the direct potentiometric method can be combined with the accuracy of the titration methods, because the relatively high error of the potentiometric measurements (in range from about 2 to 4 %) occurs only in relation to a relatively low amount of the remaining part of the component to be determined or the surplus of the titration reagent (generally in the range from about 5 to 10 %). This means, the error is only in the range from abour 0,2 to about 0,4 % in relation to the full amount of the sample. The other recognition is that the potentiometric titration curves are approximately linear and show high slope in the value range differing from the end point of the titration by about $\pm$10 % and this can be the basis of a reliable control process ensuring high accuracy.

The analysis of the recognition given above resulted in a further recognition: the proposed method of carrying out the measurements renders the measurements of such components possible which can be determined only by application of a suprlus of the titration reagent and following titration of this surplus with another titration reagent.This second

step is in the case of such components not necessary because of replacing it by the direct potentiometric measurement without the danger of apppreciable lowering the accuracy of the determination.

The object of the invention is therefore to provide a method and an equipment whereby it is possible to avoid the disadvantages of the potentiometric metering methods in the environment of the end point potential (as the uncertainity of detecting this point etc.) with ensuring a result of high accuracy being obtainable also in form of an electric signal, wherein the electric signal can be applied for realising a reliable control process especially for industrial purposes.

The invention proposes therefore a process and an equipment which are applicable to determining concentration of a component of a liquid sample by means of potentiometry. In the proposed method, comprising the steps of admixing a titration reagent of known concentration in regulated quantities to a sample of known quantity, measuring the potential of an electrode contacting the liquid sample including the admixed titration reagent and determining the concentration on the basis of the measured potential, the novelty lies in application the further steps of admixing the titration reagent in a quantity deviating from the aequivalence quantity by about 1 % to about 20 %, advantageously by about 4 % to about 10 % in weight, homogenising, if necessary, the liquid received by admixing, determining the difference to the aequivalence quantity by carrying out a measurement of the electric potential of the electrode and comparing the measured potential value with a calibration diagram determined earlier and computing the concentration on the basis of the difference determined taking into account the quantity of the titration reagent admixed to the liquid sample.

The method of the invention is advantageously applicable for determining the concentration of a component de-

composing in the pH value range of the analysis when the titration reagent is applied in the quantity exceeding the aequivalence quantity.

The method of the invention is especially advantageously applicable to methods of flow analysis.

The equipment proposed by the invention includes a unit for receiving a liquid sample, a feeding unit for introducing a titration reagent into the liquid sample and measuring means containing an electrode held with the liquid sample mixed with the titration reagent. The novel element of the equipment is a mixer for homogenising the liquid sample, wherein the feeding unit introduces a regulated quantity of a liquid into the sample and the measuring means are connected to a linear amplifying and/or regulating unit. For introducing the regulated quantities it is advantageous to apply a peristaltic pump, because of high accuracy of feeding realised by it. The results of the measurements can be simply generated, if the measuring unit is equipped with a computing unit which is capable of generating a control signal for regulating the feeding of a liquid to a technological process.

The essence of the invention is hence the setting a working point differing from the aequivalence point expressed in concentration units by at most ± 20 %. This is especially advantageous from the point of view that the disadvantageous electrode features coming out in the environment of the end point potential can be avoided. This disadvantage is e.g. the low process of establishing the potential value, the low reproducibility of the measurement results.

It is a further advantage that the high slope of the characteristics simplifies the realisation of the control processes: instead of logarithmic amplifiers the regulators can be of proportional (linear) types, wherein the small copcentration changes cause big and approximately linear changes of the output signals.

On determining concentration values in flowing samples it is a further advantage of the invention that the high oscillation of the concentration, often detectable at the beginning of the control process, can be avoided, because of introducing even in the first step a quantity of the reagent which follows from the computing step giving an approximate value.

The invention will be further described in detail with reference to the accompanied drawings and to preferred embodiments shown by way of example. In the drawings

Figure 1 shows the block diagram of realising the method of the invention in general case, and

Figure 2 shows the blok diagram of realising the method of the invention in case of analysis to be carried out in flowing samples.

During carrying out the method of the invention the substances should be applied in stable and/or well known quantities, according to the general principles of the chemical analysis. According to this a given quantity of a titration reagent is introduced to a given quantity of a solution comprising a component the concentration of which should be determined (of course, the quantity of this component can be also the object of the measurement). After introducing the necessary amount of the titration reagent the next step is to carry out a direct potentiometric measurement. By the last the potential of a measuring electrode can be established, the measuring electrode connecting the liquid resulted by the introducing step mentioned above. On the basis of the measured potential value, taking into account a calibration curve determined earlier it is possible to determine the concentration of the given component.

By maintaining both the solution to be investigated and the titration reagent in steady flow the conditions of realising the method of the invention are especially advantageous. In this case the sample of steady volume flow rate

is admixed with a solution of the titration reagent flowing also with steady volume flow rate.

The concentration of the titration reagent in the admixed solution should be selected in a way that this solution can give a titration in the range from about 90 % to 95 % or from about 105 % to about 110 % for the flowing sample solution. The solution admixed with the titration reagent should generally be homogenised (mixed with high care) and thereafter introduced into a detector chamber of a potentiometric measuring unit. The measure chamber potential as a direct potentiometric measurement should be compared with a calibration curve for determining the concentration to be established. This concentration follows from the measured value relating to the part of the sample not titrated by the titration reagent or to the surplus of the titration reagent introduced in excess amount. In the knowledge of the quantity of the titration reagent (its volume flow rate), the quantity (volume flow rate) of the sample and on the basis of the concentration of the titration reagent, taking into account the results of the direct potentiometric measurements of the not titrated amount or the surplus it is possible to determine with high accuracy the concentration of the selected component in the sample. In the case of flow analysis the results can be computed on the basis of formulae

$$\gamma_R W_R C_R + \gamma_M (W_R + W_M) C_x = \gamma_M W_M C_M$$

and in case of surplus

$$\gamma_R W_R C_R = \gamma_M W_M C_M + \gamma_R (W_R + W_M) C_x$$

wherein the meaning of the symbols is the following:

γ_R and γ_M the stoichimetric factors figuring in the equation of the characteristic chemical reaction of the titration process,

W_R and W_M the volume flow rates of the titration reagent and the sample, respectively,

C_R and C_M the concentration of the titration reagent and the sample, respectively, and

C_x the concentration of the sample not titrated by the reagent or of the surplus of the titration reagent.

Because the values of $_R$, W_R, C_R, $_M$, W_M are known with high accuracy, and C_R C_x, therefore the error made in determining the value of C_x is negligable and C_M can be determined with high accuracy.

The equipment proposed by the invention which is capable of carrying out the method explained above (Fig. 1 and 2) contains a unit 2 for receiving a sample M and it is advantageous to introduce a titration reagent R also into this unit 2. The content of the receiving unit 2 is homogenised by a mixer 4. The receiving unit 2 sends liquid 1 to measuring means 5 connected by its output to control means V including a linear amplifying and/or regulating unit L connected to a computing unit 8 and a display unit D. One or more feeding units 3 are applied for feeding the titration reagent R and the sample M to the receiving unit 2. The titration reagent R can be taken from a reagent container 7.

In the measuring means 5 the liquid 1 is connected with a measuring electrode 11 the potential of which is measured (expressed in pH or mV value). In the measuring means 5 a known per se reference electrode 10 and a thermometer 12 are applied, the last being of thermistor or conductivity type.

The control means V contain, as mentioned, a linear amplifying and/or regulating unit L for generating control signals S on the basis of signals received from the measuring means 5. The output signal of the linear amplifying and/or regulating unit L is connected to the display unit D for displaying the concentration values and to a computing unit 8 for determining further data.

During operating the feeding unit 3 made advantageously in form of a peristaltic pump 6 (Fig. 2) introduces the titration reagent R and the sample M in regulated quantity or volume flow rate. The liquid 1 homogenised by the mixer 4 is fed into the measuring unit 5 and on the basis of the output signals of the last the control means V generate control signals S, and gives by display unit D the analogous or digital value of the concentration of the component.

The object of the invention will be explained in more detail on the basis of examples given below.

EXAMPLE 1

Continuous measurement of the concentration of hydrochloric acid

The changes of the hydrochloric acid concentration were measured in a way that the hydrochloric acid to be investigated and the hydrochloric acid solution of 0,1 M concentration for titration is fed into a mixing vessel by means of peristaltic pumps and the pH value of the liquid received from the mixing vessel was measured by a glass electrode.The volume flow rate of both of liquids was about 2 ml/min. In the mixing vessel a magnetic mixer was applied to the both liquid flow. The samples of the hydrochloric acid were selected to have concentration oscillating by $\pm$4 % around the nominal value 0,109 M. The signal of the measuring unit prepared to measurements of pH value showed linear changes with good approximation up to some percent changes of the hydrochloric acid concentration (up to about $\pm$ 4%), the changes were characterized by high slope of following the concentration (about 2 mV/%).

The approximately linear range is wide enough for carrying out practical control problems.

EXAMPLE 2

Continuous measurement of chloride concentration

The means applied and the volume flow rates were the same as in the Example 1, excepting the measuring electrode

selected to be an electrode reacting selectively to chlorides and silver. The titration reagent was $AgNO_3$ solution of 0,05 M concentration and the sample NaCl solution with concentration oscillating around 0,046 M in one case and 0,054 M in the other. The issuing of the colloidal sediment was facilitated by the presence of a little amount of gelatine. The output signal of the unit for measuring pH and mV values showed linear changes up to some percent changes (about ± 4 %) of the concentration with good approximation and high slope of the change.

The further examples (Examples 3 and 4) shows some very important possibilities of application, wherein the titration reagent is intruduced in surplus.

EXAMPLE 3.

Continuous measurement and regulation of the whole acid content of zinc phosphate baths

The zinc phosphate baths applied to surface treatments are characterized mostly by the whole acid content expressed by points. According to the definition the whole acid content is reflected on a linear scale wherein 1 point corresponds to concentration 0,01 N of acids in the solution.

The whole acid content of the zinc phosphate baths was continuously measured in an arrangement according to Fig. 1. The sample and the titration reagent were transported by means of a peristaltic pump ensuring volume flow rate 2,5 ml/min. As a titration reagent the NaOH solution of 0,126 N concentration was used which has concentration with 5 % higher than the solution NaOH being aequivalent with the phosphatizing bath having whole acid content 12 points.

In order to exclude issuing of sediments a substance for generating complex compounds, e.g. Na_4EDTA was applied to basic solutions.

It was observed that the change of the whole acid content by ± 4 % caused changes in the measured pH value

following the whole acid content according to a linear function. By applying Na_4EDTA in the titration reagent solution the linear range was as wide as 7 % of the whole acid content. The slope of the linear range was in the last case about 1 pH/point. Measuring samples of steady whole acid content it was possible to state that the stability of the measured pH value was $\pm$0,02 pH/hour. The high slope and the high accuracy render realising a very reliable system for measuring and controlling the concentration possible.

EXAMPLE 4

Continuous measurement and regulation of the nitrite content of zinc phosphate baths

The nitrite concentration of the zinc phosphate baths applied to surface treatments are often characterized by acceleration points. According to the definition in a linear scale 1 acceleration point corresponds to a solution comprising nitrites in concentration 0,001 N. The measurement of the nitrites causes many problems according to the known methods because they are very instable in acidic environment.

The acceleration point value of zinc phosphate baths was determined in a measuring arrangement according to the Figure 1. The indicator electrode was made of platinum and as titration reagent the solution of 0,042 N cerium sulphate was applied in 3 N sulphuric acid (H_2SO_4).

Samples with different acceleration point value oscillating around 4 in the range of $\pm$6 % were prepared and the potential of the measuring electrode was measured. The dependence of the measured values was observed to be linear and characterized by high slope (about 250 mV/point, corresponding to about 10 mV/%), and these factors allowed to realise a control system working with high sensitivity and accuracy.

By applying a titration reagent in solution stronger than the aequivalence the error arising from decomposing the nitrites in acidic environment can be avoided and the

danger of applying two much reagent can be diminished.

The method and the equipment as proposed by the invention can be applied in the processes of chemical analysis, in controlling industrial processes, as maintaining the steady composition of phosphatizing baths, regulating the composition of galvanizing baths and for many other purposes, wherein the quick determination of the concentration of a component is important without very high requirements as for the accuracy but with accuracy high enough for practical industrial control applications.

However the method was shown above with reference to some specific kinds of applications, it is obvious that on the basis of the disclosure the skilled artisan can prepare many other possibilities of application falling within the scope of protection defined by the appended claims and the description.

CLAIMS:

1. Method of determining concentration of a component of a liquid sample by means of potentiometry, comprising the steps of admixing a titration reagent of known concentration in regulated quantities to a sample of known quantity, measuring the potential of an electrode contacting the liquid sample including the admixed titration reagent and determining the concentration on the basis of the measured potential, characterized in further steps of admixing the titration reagent in a quantity deviating from the aequivalence quantity by about 1 % to about 20 % in weight, homogenising, if necessary, the liquid received in the admixing step, determining the difference to the aequivalence quantity by carrying out a measurement of the electric potential of the electrode and comparing the measured potential value with a calibration diagram determined earlier and computing the concentration on the basis of the difference determined taking into account the quantity of the titration reagent admixed to the liquid sample.

2. The method according to claim 1, characterized in admixing the titration reagent in a quantity deviating from the aequivalence quantity in weight by about 4 % to about 10 %.

3. The method according to claim 1 or 2, characterized in admixing the titration reagent in a quantity lying under the the aequivalence quantity.

4. The method according to claim 1 or 2, characterized in admixing the titration reagent in a quantity exceeding the aequivalence quantity.

5. The method according to any of claims 1 to 4, characterized in maintaining the liquid sample in flow and admixing the titration reagent in form of a liquid current.

6. Equipment for determining concentration of a component of a liquid sample by means of potentiometry, compris-

ing a unit for receiving a liquid sample, a feeding unit for introducing a titration reagent into the liquid sample and measuring means including an electrode held in contact with the liquid sample containing the titration reagent, characterized in further comprising a mixer (4) for homogenising the liquid sample, wherein the feeding unit (3) introduces a regulated quantity of a liquid into the sample and the measuring means (5) are connected to a linear amplifying and/or regulating unit (L).

7. Equipment according to claim 6, characterized in comprising a peristaltic pump (6) for intruducing the liquid sample (M) and the titration reagent (R) into the mixer (4).

8. Equipment according to claim 6 or 7, characterized in further comprising control means (V) for receiving the output signals of the linear amplifying and/or regulating unit (L), the control means (V) including a display unit (D) for demonstrating a signal proportionally to the deviation from a nominal concentration value.

9. Equipmenent according to any of claims 6 to 8, characterized in further comprising a computing unit (8) connected to the linear amplifying and/or regulating unit (L).

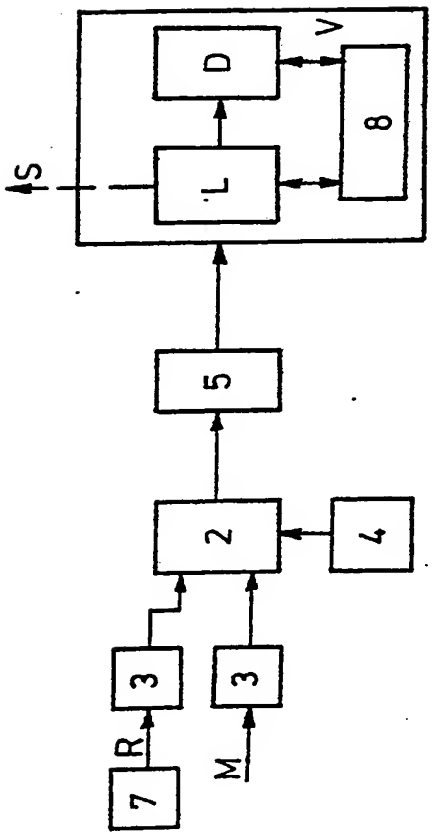


Fig.1

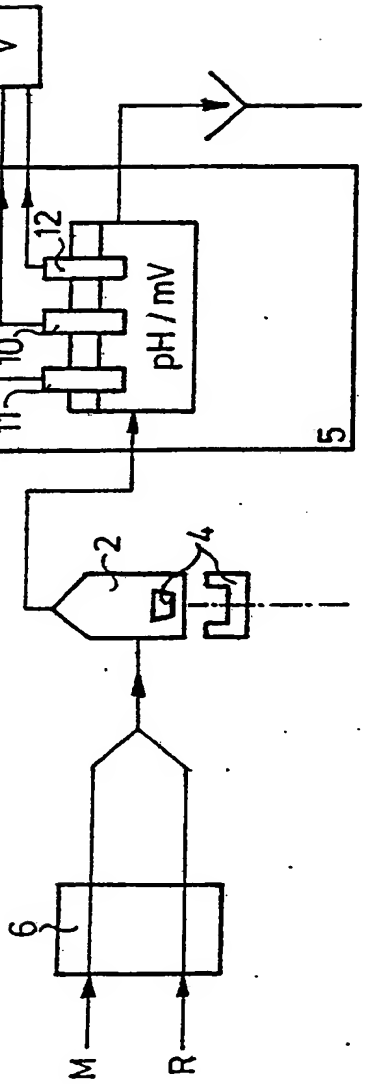


Fig.2

INTERNATIONAL SEARCH REPORT

International Application No PCT/HU 88/00007

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[4]: G 01 N 31/16, 27/26

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
Int.Cl.[4]	G 01 N 31/16,27/26

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	DE, B, 2 716 560 (RADELKIE ELEKTROKEMIAI MÜSZERGYARTO SZÖV.) 25 October 1979 (25.10.79).	(1,2,4-9)
X	CH, A, 431 444 (POLYMETRON AG) 31 August 1967 (31.08.67).	(1-9)
A	CH, A, 497 699 (ZELLWEGER AG) 30 November 1970 (30.11.70).	(1-9)
A	GB, A, 1 421 223 (E.I. DU PONT) 14 January 1976 (14.01.76).	(1-9)

---

* Special categories of cited documents: [10]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
13 April 1988 (13.04.88)	19 April 1988 (19.04.88)
International Searching Authority	**Signature of Authorized Officer**
AUSTRIAN PATENT OFFICE	Pippmann

Anhang zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

Annex to the International Search Report on International Patent Application No. PCT/HU 88/00007

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned International search report. The Austrian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Annexe au rapport de recherche internationale relatif à la demande de brevet international n°.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche internationale visé ci-dessus. Les renseignements fournis sont donnés à titre indicatif et n'engagent pas la responsabilité de l'Office autrichien des brevets.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
DE-B -2 716 560	25/10/1979	DK-A - 1 718/77	21/10/1977
-A1-	03/11/1977	DK-B - 149 318	28/04/1986
-C3-	17/07/1980	DK-C - 149 318	15/09/1986
		GB-A - 1 557 392	12/12/1979
		HU-P - 174 711	28/03/1980
		IT-A - 1 081 360	21/05/1985
		JP-A2-52-128 195	27/10/1977
		JP-B4-57-056 692	01/12/1982
		US-A - 4 120 657	17/10/1978
CH-A - 431 444	31/08/1967	None	
CH-A - 497 699	30/11/1970	DE-A - 1 965 225	01/04/1971
		DE-B2- 1 965 225	29/06/1978
		FR-A5- 2 060 472	18/06/1971
		GB-A - 1 306 811	14/02/1973
		SE-B - 376 088	05/05/1975
		SE-C - 376 088	14/08/1975
		US-A - 3 717 435	20/02/1973
GB-A -1 421 223	14/01/1976	None	